

SCIENCE FOR CERAMIC PRODUCTION

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SYNTHESIS OF HIGH-TEMPERATURE PHASES ON VERMICULITE FILLER

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The results of research on the modification of exfoliated vermiculite by activated silica, obtained from raw vermiculite by acid treatment, are presented. It is shown that at annealing temperatures 1100 – 1200°C a high temperature phase (cristobalite) forms in the phase composition of the material obtained. The properties and phase composition of the ceramic vermiculite samples fabricated on the basis of modified vermiculite and refractory clay are presented.

Key words: vermiculite, high-temperature phases, ceramic vermiculite.

High-temperature heat-insulation materials based on exfoliated vermiculite with different kinds of binder are used in domestic and foreign practice. The operating temperature of such articles, depending on the binder used, is not more than 1100°C and 1200°C for short-time heating. In domestic practice molded heat-insulation materials based on ceramic and modified silicate-ash binders are mostly used in the lining of industrial heating units. Of the many proposed heat-insulation materials based on exfoliated vermiculite only materials with an enclosing refractory matrix are considered for use at working temperatures above 1000°C [1, 2].

It is known that to obtain heat-insulating vermiculite articles using a clay binder the main phases making the material refractory are mullite and cordierite [1]. However, the technology for obtaining a material with high cordierite content and high melting temperature and ensuring a high operating temperature provides long soaking times at temperature 1250 – 1350°C but not high operating temperatures. For this reason the pressing problems of obtaining heat-insulating vermiculite articles are the reduction of the temperature and time required to synthesize the material with formation of high-temperature phases, securing operating temperatures above 1200°C, inside a ceramic matrix.

High-temperature materials with a ceramic refractory matrix have been under development since the end of the 1930s. Publications of an applied nature started to appear in the second half of the 1960s. These works culminated in the development of a wide range of vermiculite heat-insulation materials with a mineral binder and the development of a technology for producing such articles using the methods of plastic and semidry molding. The properties of the materials developed were as follows: apparent density 400 – 600 kg/m³; maximum strength in bending 0.49 – 0.56 MPa, additional linear shrinkage 0.06 – 0.8% at temperature 1150°C and thermal conductivity of the articles obtained 0.09 – 0.16 W/(m · K) at average temperature 350°C and 0.11 – 0.18 W/(m · K) at average temperature 650°C. The maximum usage temperature is 1150°C [3].

The key idea in the development of high-temperature heat-insulation materials based on vermiculite was the concept composition – structure – property. Exfoliated vermiculite from Kovdorslyuda JSC with the fraction 1.2 – 2.0 mm was used as the filler. The chemical composition of the raw vermiculite (content, wt %) was as follows: 34.38 SiO₂; 11.22 Al₂O₃; 6.70 (ΣFeO + Fe₂O₃); 1.24 CaO; 24.82 MgO; 0.56 TiO₂; 0.27 K₂O; 0.11 Cr₂O₃; 0.06 MnO; 0.05 NiO; 0.08 SO₃; and, 20.50 LOC.

The choice of the fractional composition of the vermiculite used was based on the following factors:

– vermiculite with fraction greater than 5 mm and mixing of the molding body is crushed and acquires excess moisture; during firing it re-exfoliates, which results in lower strength and even the destruction of the sample;

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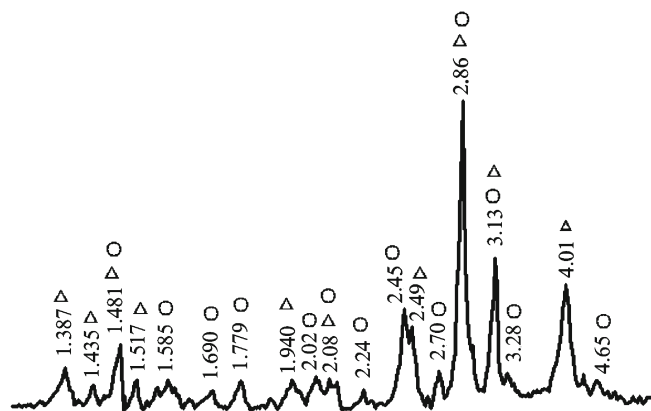


Fig. 1. X-ray diffraction pattern of vermiculite filler modified by activated silica at firing temperature 1100°C: O) enstatite; Δ) cristobalite.

– vermiculite with fraction less than 0.5 mm is also undesirable, because it increases the density and decreases the porosity of the sample; the optimal fractions are 1.2 – 2.5 or 2.5 – 5.0 mm.

The choice of interval for high-temperature treatment of the initial vermiculite (1000 – 1200°C) for complete removal of interlayer water and formation of enstatite structure was limited by the temperature stability of vermiculite: sintering temperature 1260°C and melting temperature 1315 – 1350°C.

The purpose of our investigations was to obtain high-temperature phases separately based on vermiculite filler, which is poorly given to subsequent thermochemical transformations, and on organic refractory clay (used as a binder) as a phase capable of further structure transformation. In addition, the problems of modifying the filler and binder were considerably different. Having acquired temperature stability, the vermiculite filler should preserve the packet structure determining its heat-shielding properties.

Phase formation with the packet structure being preserved during heat-treatment of vermiculite has been studied repeatedly, including in a mixture with the binder, but there was no specific objective to obtain material with high utilization temperature [3]. The clay binder must acquire to the maximum degree possible refractory properties with additional porosity being imparted at the same time. For the standpoint of conserving resources it is desirable to modify the filler and the binder in a single system and in one process cycle. The methods and procedures developed and the result obtained are presented below.

It follows from the chemical composition of vermiculite presented that it is inadequate for synthesizing inside a ceramic matrix new high-temperature phases, except for phases which are already known (enstatite). For this reason, to obtain additional phases the vermiculite was modified by activated silica obtained from the raw vermiculite. Raw vermiculite was treated with 20% sulfuric acid with heating to 60°C over 1 h. The product obtained was washed with dis-

tilled water to a neutral reaction and dried to constant mass. The content (by weight) of activated silica in the product obtained was up to 98%.⁶ It was added to the batch with vermiculite in the amounts 15 and 20%. The mixture was pressed and fired at temperature 1000 – 1200°C. It was determined that at firing temperature 1000°C the phase composition of the synthesized material is represented mainly by enstatite; no silicon oxide reflections are observed. At firing temperature 1100 – 1200°C cristobalite appears in the phase composition in addition to enstatite (Fig. 1); the cristobalite phase is a higher temperature phase than enstatite.

An examination of the samples under a microscope showed that the silicon-containing phase is located along the edges of the vermiculite filler. Carbothermic reduction of silicon oxide was conducted in order to create a temperature stable framework so that the silicon-containing phase is uniformly distributed over the surface of the vermiculite.

For this the vermiculite was mixed with silicon oxide and carbon in amounts required for the carbothermic reduction of all silicon oxide in the vermiculite. On the basis of previous studies [4] it was supposed that as a result of the partial carbothermic reduction of silicon oxide SiO_2 from the solid phase the SiO_2 will migrate in the form of SiO gas through the ceramic matrix followed by synthesis of thermodynamically allowed structures. Similar migration of other components is also possible with the same effect.

To obtain a uniform mixture the silicon oxide and carbon were premixed in a vibratory grater for 1 min. The mixture obtained was added into the vermiculite and remixed. The mixtures obtained were fired at 1100°C in oxidizing and reducing (in carbon filler) media. The firing regime consisted of raising the temperature to 400°C (2.5 h) and then to 1100°C at the rate 200 K/h with isothermal soaking at the maximum temperature for 1 and 2 h. The phase composition of the materials was investigated by XPA.

The formation of cristobalite predominately starts when vermiculite is fired in an oxidizing medium with 15 wt.% mixture of carbon and silicon oxide with isothermal soaking for 1 h (Fig. 2). The content of enstatite is negligible. As the content of the mixture of carbon and silicon oxide increases to 20% the phase composition remains practically unchanged.

When the soaking time was increased to 2 h it was found that firing vermiculite with 15% mixture of carbon and silicon oxide produced practically equal quantities of enstatite and cristobalite (see Fig. 2). The cristobalite content increases very little when the amount of mixture is increased to 20%.

The phase composition of vermiculite fired for 1 h with 15% amount of the mixture of carbon and silicon oxide in the carbon filler is represented mainly by quartz and cristobalite as well as a very small amount of enstatite. For soaking time 2 h the content of enstatite and cristobalite is almost twice as

⁶ Here and below, unless stipulated otherwise, the content by weight, %.

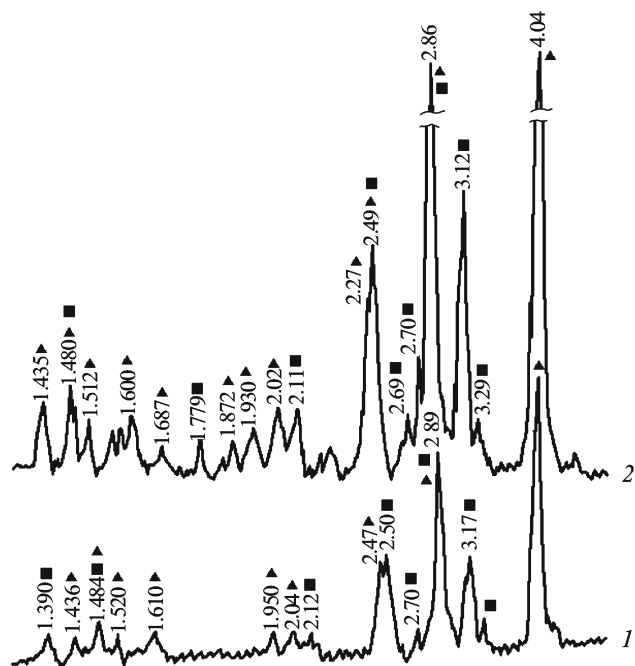


Fig. 2. X-ray diffraction pattern of fired vermiculite with 15 wt.% ($\text{SiO}_2 + \text{C}$), firing temperature 1100°C : 1) soaking at final temperature 1 h; 2) 2 h; ■) enstatite; ▲) cristobalite.

large as that obtained with 1 h (Fig. 3). Increasing the content of silicon oxide in the mixture to 20% significantly increases the amount of cristobalite compared with enstatite.

To obtain ceramic vermiculite modified by a mixture of silicon oxide and carbon the vermiculite was mixed with refractory clay in the ratio 1 : 2 and 3×3 cm cylindrical samples were molded by the plastic and semidry methods. A 3% solution of polyvinyl alcohol was used to moisten the mixture to fabricate samples by semidry pressing. The moisture content of the mixture was 50.7 – 52.8% for plastic molding and 11.4 – 12.5% for semidry molding. The firing temperature of the samples was $1000 - 1100^\circ\text{C}$.

Refractory clay from the Borovichsko-Lyubytinskaya group of deposits was used as the binder. The main component of these refractory clays is kaolinite, characterized by high dispersity, which predetermines the high plasticity of the raw material. The plasticity number of the clay used is 18 – 23, the molding moisture content is 28 – 42% and the refractoriness is 1680°C . The chemical composition of the clay is (%): 34.89 Al_2O_3 ; 2.19 Fe_2O_3 ; 57.34 SiO_2 ; 0.8 CaO; 0.7 MgO; 2.16 TiO_2 ; 1.22 ($\text{Na}_2 + \text{K}_2$); and, 0.7 LOC.

Kaolinite undergoes mullitization when heated. Mullite is distinguished by high melting temperature and elevated mechanical strength. It is known that mullite forms in the two-component system $\text{Al}_2\text{O}_3 - \text{SiO}_2$ at temperatures above 1400°C . In systems with three or more components, containing K_2O , Na_2O , CaO, F and TiO_2 , which are always present in natural initial materials, the formation temperature of mullite decreases because the reactions are accelerated as a

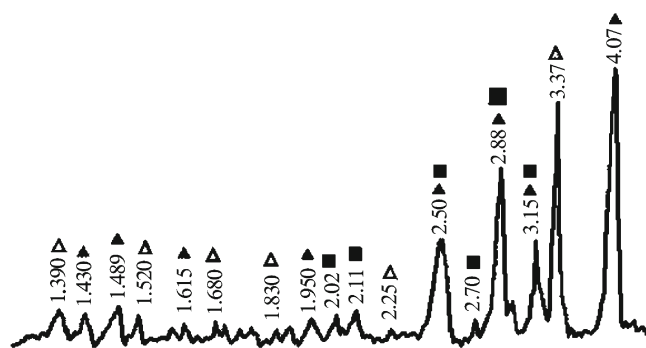


Fig. 3. X-ray diffraction pattern of vermiculite fired with 15 wt.% ($\text{SiO}_2 + \text{C}$) in carbon filling, firing temperature 1100°C with 2 h soaking at the final temperature: ■) enstatite; ▲) cristobalite; Δ) quartz.

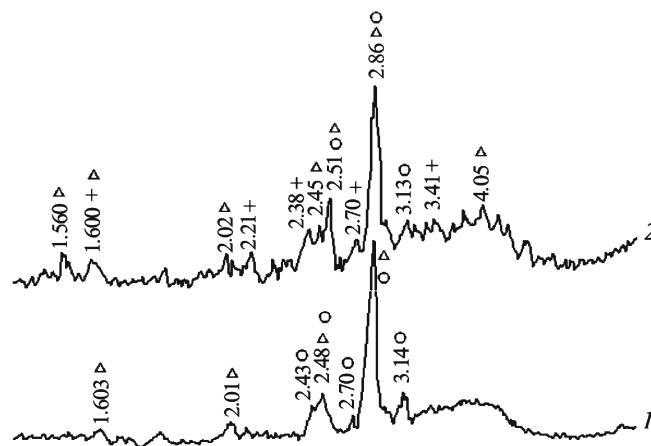


Fig. 4. X-ray diffraction pattern of samples of ceramic vermiculite from plastic (1) and semi-dry (2) formation, fired at 1100°C : O) enstatite; Δ) cristobalite; +) mullite.

result of the appearance of a liquid phase at relatively low temperature [5].

In studying the phase composition of samples based on vermiculite and kaolinite after firing it was found that at 1000°C it is represented by cristobalite and enstatite. No reflections due to the initial kaolinite or the products of its mullitization are observed. This shows that when mixed with water kaolinites transform into an amorphous phase with aluminum oxyhydrates being formed and the initial structure partially preserved. The main initial structure of kaolinites is an extended layer of SiO_4^{4-} , formed by oxygen-silicon tetrahedra joined into a hexagonal network, and a gibbsite layer ($\text{OH}_6 - \text{Al}_4 - (\text{OH})_2\text{O}_4$). The same basic structure is characteristic for clay minerals of the montmorillonite group, which also contain magnesium and for which mullite and cordierite characteristically form at about 1200°C [6].

Actually, at firing temperature 1100°C mullite starts to form in samples formed by semidry molding (Fig. 4). At firing temperature 1200°C phase transformations in the clay in-

TABLE 1. Physical and Mechanical Properties of Fired Material Based on Modified Vermiculite and Refractory Clay

Batch No.	SiO ₂ additive, wt. %	Air shrinkage, %	Fire shrinkage, %		Strength in compression, MPa		Density, kg/m ³	
			at firing temperature, °C					
			1000	1100	1000	1100	1000	1100
Plastic molding								
1	15	5.4	2.9	3.7	2.7	3.8	650	730
2	20	3.7	2.1	4.7	2.9	4.0	700	740
Semidry pressing								
1	15	0.6	3.0	3.7	2.8	3.3	700	1110
2	20	0.6	2.9	3.5	3.3	4.2	800	1230

TABLE 2. Thermal Conductivity of Samples Formed by Different Methods

Silicon oxide content, wt. %	Thermal conductivity* of samples, W/(m · K), fired at temperature, °C			
	Semidry pressing		Plastic molding	
	1000	1100	1000	1100
15	0.112	0.118	0.110	0.112
20	0.114	0.120	0.102	0.116

* Determined at average temperature 20°C.

crease the mullite content. At these temperatures mullite is not present in samples obtained by plastic molding. In order for a cordierite phase to form in the experimental samples the amount of magnesium in the batch must be increased by introducing magnesium-containing additives.

The physical-mechanical and thermophysical properties of samples obtained by semidry molding were studied. The results are presented in Tables 1 and 2. It was determined that increasing the amount of the SiO₂ additive to 20% increases the density, strength and fire shrinkage very little at all firing temperatures as compared with the addition of 15% SiO₂. The same behavior is observed in pressed samples. It should be noted that compared with samples obtained by plastic molding the density of pressed samples is 1.5 times higher and the thermal conductivity is higher. They are also characterized by lower air shrinkage.

In summary, it was determined that the modification of vermiculite by activated silicon and carbothermic reduction of silicon oxide result in the formation of high-temperature phases, which opens up the prospects for obtaining vermiculite filler that can be used as 1200 – 1300°C.

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